Reactions of Ketene with Phenol, Resorcine, Phloroglucine and Dimedone

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NOTES

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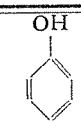
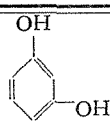
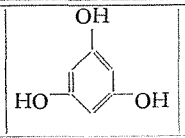
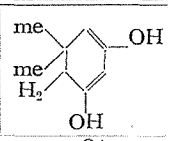
The reactions of ketene with phenol, resorcine, phloroglucine and dimedone have been studied.

(1) Without catalyst, ketene gave always O-acetyl derivatives of them.

(2) With sulfuric acid, pyridine or sodium acetate as catalyst, O-acetyl de-

Table 1. Reactions of ketene with phenol, resorcine, phloroglucine and dimedone.

Catalyst	(1) React. Temp.	Phenols / Products				
None	Low	Name(2)(3)	O	—	×	O*
		Yield(4)	80			55
	High	Name	—	O(mono), O(di)	O(tri)	O*
		Yield		67, 98	2	72
Na (5) Salt	Low	Name	O*	—	O(tri)	O*
		Yield	68		29	61
	High	Name	O*	O*(mono, di)	resine	O*
		Yield	74	78		61
H_2SO_4	Low	Name	O	—	resine	×
		Yield	85			
	High	Name	—	O(di)	resine	resine
		Yield		77		
	Low	Name	O	—	O(tri)	×
		Yield	87		14	
	High	Name	—	O(di)	O(tri)	O*
		Yield		88	26	61
AcONa	Low	Name	—	—	—	×
		Yield				
	High	Name	—	—	—	O*
		Yield				44

(1) React. Temp.: Low—Cooling with ice or room temp. (solvent: ether).
High—*Warming on a steam bath* (solvent:benzene).

(2) O : O-acetyl derivative.
O(mono) : O-mono-acetyl derivative.
O(di) : O-di-acetyl derivative.
O(tri) : O-tri-acetyl derivative.
O* : O-acetyl derivative with a small amount of C-acetyl derivative, which seems to be present although not confirmed.

(3) × : No reaction.

(4) Yield (%) : Theoretical yield.

(5) Na-Salt : Treated with 20% H_2SO_4 after the reaction.

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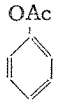
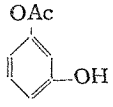
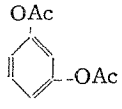
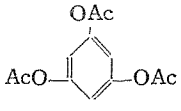
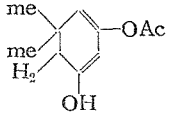
rivatives were produced.

(3) In the reactions with their sodium salts, O-acetyl derivatives were produced, containing a small amount of C-acetyl derivatives.

Some experimental results were cited in Tables 1 and 2.

Table 2. Some physical constants of O-acetyl derivatives obtained from phenol, resorcine, phloroglucine and dimedone.

O-acetyl derivative	Physical properties		
	m.p. (°C)	b.p. (°C)	n_D^{20}
	—	111 (60 mm.)	1.5200
	—	135-7 (7 mm.)	1.5328
	—	130-1 (7 mm.)	1.5034
	105-7	—	—
	—	128-132 (15 mm.)	1.4814

Reaction of Ketene with Ethyl Acetoacetate in the Presence of Pyridine

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In the presence of a very small amount of pyridine, ketene was reacted with ethyl acetoacetate above -20°C, and a reaction product rich in O-acetyl- (II), poor in C-acetyl ethyl acetoacetate (I), was obtained.

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